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VIA ELECTRONIC MAIL

April 25, 2011

Erin Foresman
US Environmental Protection Agency
75 Hawthorne Street
San Francisco, CA 94105

Subject: Water Quality Challenges in the San Francisco Bay/Sacramento-San Joaquin Delta Estuary (Document ID EPA-R09-OW-2010-0976-0001)

Dear Ms. Foresman,

The Western States Petroleum Association (WSPA) is a non-profit trade association representing twenty-six companies that explore for, produce, refine, transport and market petroleum, petroleum products, natural gas and other energy supplies in California, Arizona, Nevada, Oregon, Washington and Hawaii.

In response to the Advanced Notice of Proposed Rulemaking (ANPR) for Water Quality Challenges in the San Francisco Bay/Delta Estuary (Bay Delta Estuary), we are providing the attached comments.

The focus of our comments pertains to selenium in the Bay Delta Estuary. The San Francisco Bay Regional Water Quality Control Board has completed preliminary efforts on their development of the North San Francisco Bay Selenium Total Maximum Daily Load (TMDL). The TMDL incorporates several documents that are included as supporting documents to our comments: Technical Memorandum 2 (TM-2) Selenium Data Summary and Source Analysis; Technical Memorandum 3 (TM-3) Toxicological Assessment; and, Technical Memorandum 6 (TM-6) Simulation of Selenium Fate and Transport.

In addition, the North San Francisco Bay Selenium Characterization Study (Study) is currently underway, and the work plan is included as a supporting document. This Study in conjunction with the results presented in TM-6 provides the basis for a reevaluation of selenium speciation in the Bay after a data collection gap of nearly 10 years.

The information from the TMDL and Study indicates that the ratio of particulate to dissolved selenium concentrations (Kd) cannot be assumed to remain fixed over changing conditions, which may include, among other things, changing sources, phytoplankton abundance and species, selenium speciation, and also seasonal and long term hydrological changes. The transformations and uptake of various selenium species in the Bay Delta Estuary have been shown to be dynamically complex, and thus the use of a simple predictive tool to assess uptake would not be appropriate.

The model developed in the TMDL has demonstrated the ability to predict selenium concentrations in the water column and associated bioaccumulation in water body biota. The model was verified using clam data collected from 1995 – 2010 and was shown to accurately simulate the long-term record of selenium in the clam *Corbula amurensis*; this clam is described in the ANPR as a selenium-sensitive species. The ability to explain these clam data is a key advantage of the use of a more process oriented model that can be applied in settings where there are many changing factors, and where the assumption of a constant Kd ratio is not valid.

The attachments to our cover letter provide greater detail on these and other key issues we believe are vital to establishing a more accurate understanding for any proposed regulatory development pertaining to selenium in the Bay Delta Estuary that EPA may consider. Our comment package incorporates a Summary of Responses (Summary) to the three questions posed in the ANPR, detailed comments that provide expanded content to the Summary, and supporting documents from the Selenium Characterization Study and the TMDL.

We look forward to EPA's review of our comments, completing its evaluation, and providing the results of its review to the public. Thank you for this opportunity to provide input on this important matter.

Sincerely,

Kevin Buchan

Attachments:

Supporting Information in Response to Water Quality Challenges in the San Francisco Bay/Sacramento-San Joaquin Delta Estuary, Unabridged Advanced Notice of Proposed Rulemaking

North San Francisco Bay Selenium Characterization Study Plan (2010 – 2012)

Technical Memorandum 2. North San Francisco Bay Selenium Data Summary and Source Analysis

Technical Memorandum 3. North San Francisco Bay Selenium Toxicological Assessment

Technical Memorandum 6. Application of ECoS3 for Simulation of Selenium Fate and Transport in North San Francisco Bay

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Supporting Information in Response to Water Quality Challenges in the San Francisco Bay/Sacramento-San Joaquin Delta Estuary, Unabridged Advanced Notice of Proposed Rulemaking

Prepared by Tetra Tech, Inc.

April 25, 2011

Summary of Responses

A review of the information summarized by the U.S. Environmental Protection Agency (EPA) within the Selenium Program Area of the *Unabridged Advanced Notice of Proposed Rulemaking* is presented in the attached technical document. Detailed responses are presented for three questions presented by EPA for public comment. New information, contributing to the understanding of the behavior of selenium in the Bay Delta Estuary, is presented from the ongoing North San Francisco Bay Selenium Characterization Study. This study will continue through 2012 and will provide vital new information on the sources of selenium and the seasonally-influenced physical and chemical factors that affect selenium behavior in the Bay Delta Ecosystem. As part of the supporting activities provided for the development of a selenium TMDL for North San Francisco Bay, a numerical model of selenium fate and transport has been developed. This model accounts for the complex behavior of dissolved and particulate selenium in the Bay Delta Estuary and accounts for the relative efficiency of food webs in concentrating selenium. Within the technical responses below, the results of new model simulations are presented that accurately simulate the long-term record of selenium in the clam *Corbula amurensis*, described in the ANPR as a selenium-sensitive species. The responses to the posed questions also include recommendations for data needed to track selenium impacts in the Bay Delta Ecosystem. These data needs include 1) Delta selenium concentrations, 2) *Corbula amurensis* selenium concentrations and abundance, 3) particulate selenium concentrations at the ocean boundary, 4) selenium concentrations in higher trophic levels, and 5) a sustained selenium modeling framework. Additionally, this response provides a review of existing toxicity data interpretations and presents information regarding selenium's protective effects related to methylmercury toxicity.

Summary of Question Responses

1.0 What, if any, additional information is available to better characterize selenium sources, loadings and impacts within the watershed of the Bay Delta Estuary?

New Selenium Source Characterization Data

The *North San Francisco Bay Selenium Characterization Study (2010–2012)* is underway with the second of four sampling events completed in March 2011. Three types of samples are collected and analyzed: (1) Transect samples collected along a salinity gradient in the estuary, including locations in the Sacramento and San Joaquin Rivers, (2) Refinery effluent receiving-water samples collected near the effluent outfall to characterize near-field selenium concentrations and speciation; and, (3) Refinery effluent samples collected at a fully treated effluent discharge location.

The new data collected in the Selenium Characterization Study provide the basis for a major reevaluation of selenium speciation in the bay after a gap of 10 years. The data obtained in this work can be compared directly with the prior sampling, and allow interpretation of changes over the preceding decade. The preliminary findings show that Kd values, representing the ratio of particulate to dissolved concentrations, are lower in 2010 than in 1999 by a factor of 2 to 3 (Figure ES-1). This is a significant finding and demonstrates the complexity of selenium uptake by different living and non-living particulate phases. These calculations show:

- that any given snapshot of selenium distribution in different compartments should be treated with caution, and
- that the ratio of particulate to dissolved cannot be assumed to remain fixed over changing conditions, which may include, among other things, changing sources, phytoplankton abundance and species, selenium speciation, and also seasonal and long term hydrological changes.

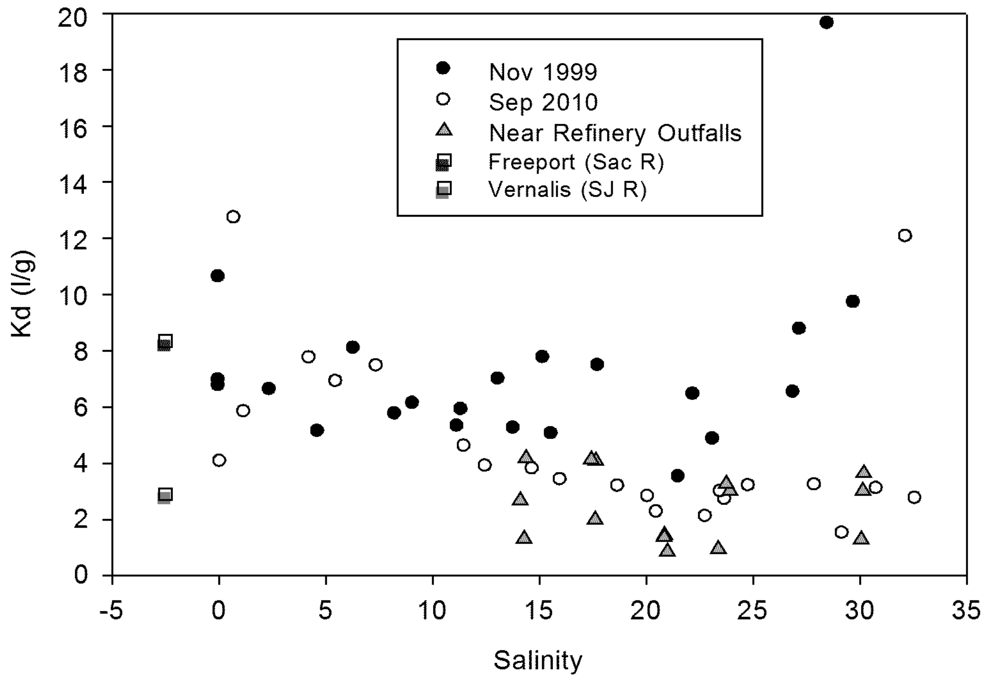

Figure ES-1. Ratio of particulate to dissolved selenium concentrations (expressed as Kd) across the estuary with data from November 1999 and September 2010.

Existing Toxicity Data and the Evaluation of Selenium Impacts

With the effort that is underway by EPA to develop a water quality criterion based on fish tissue concentration, it is important to take a critical look at the key studies that contribute to the selenium toxicity information in general and the information for species considered for evaluation of selenium exposure risk in the Bay Delta. Toxicity information for two species, white sturgeon (*Acipenser transmontanus*) and Chinook salmon (*Oncorhynchus tshawytcha*) is presented in the detailed response to questions. Additionally, new information is presented on the potential protective effects of selenium against methylmercury toxicity. The primary findings are:

- Unpublished laboratory studies using the white sturgeon have established a link between Se in parental fish tissue being transferred to eggs and larvae and resulting in substantial deformities at concentrations above about 25 ug/g. Based on these same

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studies, some investigators have attempted to identify either effect levels or No Observable Effect Concentrations (NOECs) that inherently have high variability and are not defensible based on the data reported.

- The USFWS has concluded that a tissue concentration in the Chinook Salmon of 7.9 µg/g would result in 15% mortality within 10 days. There are several issues associated with this interpretation of previously published data identified in the full response to questions. Further, it is not defensible to base a criterion on a 15% effect because this is statistically and ecologically highly uncertain.

- Dietary selenium has been shown to provide protective effects against methylmercury toxicity. There is a high binding affinity between selenium and mercury, and the mercury-selenium complexes formed have low solubility. As a result, the mercury-selenium present in tissues of prey species may not be available for dietary absorption. This relationship between mercury and selenium should be investigated further in the characterization of selenium impacts in the Bay Delta.

2.0 What data, studies, and analytical techniques (for example, models) could be used to improve our understanding of the physical processes, including surface-groundwater interactions, controlling selenium mobilization and transport to and within the Bay Delta Estuary?

Selenium exists in multiple dissolved and particulate species, with transformations between them. In the Bay Delta Estuary, these transformations are overlaid on variable riverine and tidal influences. Of the different species, particulate selenium species are of most interest, due to its sequestration by clams, and further uptake by predator organisms. Selenium speciation and thus biological uptake varies on annual and seasonal time scales. Simple representations have been proposed for biological uptake, principally by assuming that particulate selenium is a ratio of the dissolved selenium (represented as a value of Kd, as noted in the answer to the previous question). However, this approach does not capture the changing selenium speciation in the Bay and does not explain the variations in clam concentrations that have been observed over the last 15 years. Given this limitation, the simple Kd-based approach may not be able to project future clam concentrations, especially when there are changes in the hydrologic drivers, such as modifications in the flows through the Delta, or changes in the mix of Sacramento and San Joaquin River inflows.

In support of the North San Francisco Bay (NSFB) Selenium TMDL, a more detailed evaluation of the selenium fate and transport processes was developed, including characterization of all known sources, and evaluation through a modeling framework that accounts for the various transformation and uptake processes. The goal of this effort was to develop a linkage between sources, water column concentrations, and biota concentrations that represents the best current understanding of underlying processes.

As a first step, loads were characterized from all known point and non-point sources, and from various existing data sources. Annual loadings from the Central Valley through the Delta are the largest source of selenium with high variability depending on total flow through the Delta. Loads in high flow years are estimated to be more than ten times higher than in low flow years. The average Delta load is estimated to be 3,962 kg/yr. Local tributaries draining both urban and non-urban areas, although contributing lower flows than the Sacramento and San Joaquin Rivers, have high selenium concentrations, and are also a large source of selenium during the wet months (estimated average load of 354-834 kg/yr). Refineries are estimated to contribute ~550 kg/yr to NSFB.

To represent selenium processes, an estuary model was used to simulate the selenium concentrations in the water column and bioaccumulation of selenium in the NSFB (ECoS3 model, Harris and Gorley, 2003). The model built upon the previous work of Meseck and Cutter (2006) and was applied in one-dimensional form to simulate several constituents including salinity, total suspended material (TSM), phytoplankton, dissolved and particulate selenium, and selenium concentrations in bivalves and higher trophic organisms. Selenium species simulated by the model include selenite, selenate, and organic selenide. The particulate species simulated by the model include particulate organic selenium, particulate elemental selenium, and particulate adsorbed selenite and selenate.

The modeling shows that dissolved concentrations vary over a narrow range in both the dry and wet weather days, and are accompanied by significant changes in the particulate selenium speciation and Kd values in space and across seasons. This is explained as follows: In the dry season, the contribution of riverine particulate selenium is small relative to the in situ generation of phytoplankton. These conditions also result in higher particulate selenium concentrations (in µg/g). In the wet season, the contribution of riverine particulates is larger relative to in situ generation, and the overall particulate composition is more mineral and lower in selenium concentration. Furthermore, the mineral-rich particulates in greater abundance during the wet season are also assimilated less efficiently by clams. Riverine contributions of particulate selenium change from year to year, with resulting changes in concentrations of particulate selenium in the Bay, i.e., wet years have a greater riverine influence, and greater abundance of mineral-Se particulates.

The model above is especially important in explaining the clam data collected from 1995-2010, and which exhibit significant seasonal and inter-annual variability. The modeled concentrations of clams are shown along with the annual data in Figure ES-2. The model was applied using measured riverine inflows, as well as using the calibrated parameters for selenium transformation based on the 1999 speciation data, and uptake rates and assimilation efficiencies for different selenium species. A reduction in point source loads, through improved refinery wastewater treatment, is also included in the model inputs. Overall, the model is able to describe key features in the clam concentration behavior accurately. Changes from the dry season (high concentrations) to the wet season (low concentrations) in each annual cycle are explained by the riverine input of mineral-Se with lower concentrations and lower assimilation efficiency. Changes in clam selenium concentrations from one year to the next are influenced significantly by hydrology, with wet years (such as 2005 and 2006) resulting in lower clam concentrations. The ability to explain this temporal clam behavior also provides insight into future changes in the Bay, where flow modifications in the San Joaquin River or the Delta may result in riverine inputs that differ from historical, both in volume and in the amount of particulate selenium represented by the relative proportion of Sacramento and San Joaquin River flows.

The use of this model addresses the need identified in Question 2 to better explain selenium processes controlling selenium mobilization and transport to and within the Bay-Delta Estuary. Although more complex than a ratio-based approach, the added benefit of explaining mechanistically an important process of selenium uptake in the system, makes this an important tool in assessing future changes over the long term.

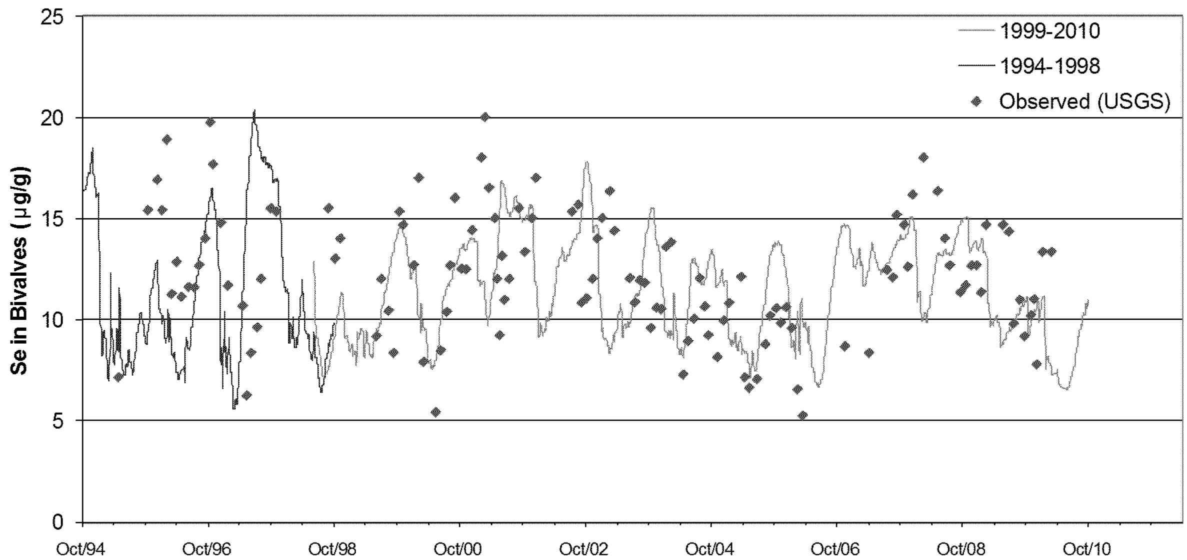

Figure ES-2 Simulated selenium concentrations in bivalve *Corbula amurensis* compared to long-term data from USGS at the Carquinez Strait for the period of 1994-2010 (Kleckner et al. 2010). Flow data used: DAYFLOW records; Refinery data used: daily data for 1999-2007, constant loads after 2007; San Joaquin River Selenium: observed data at Vernalis, multiplied by Delta removal constants.

3.0 What data are needed to track selenium impacts in the Bay Delta ecosystem as currently configured, and to evaluate potential impacts of selenium under changed flow and transport conditions into and within the Delta?

There is a critical need to develop a focused data collection effort to develop information: 1) to establish existing conditions in the Bay Delta with respect to the effects of selenium, 2) to serve as a basis for measuring change to the system, and 3) to gauge the effects of ecological forcing factors such as changes in food-web structure, flow conditions, and differences sources and forms of selenium to the system. Only recently with the implementation of the Selenium Characterization Study has there been a field sampling program devoted to supporting the development of selenium regulations. Without the collection of additional field and laboratory data, there is a risk of selecting model parameter values from sparse or incomplete data sets that support the existing concepts regarding both the relative importance of factors that affect the Bay Delta ecosystem and the existence of impairment.

The critical data needs are best classified into the following topics:

- **Delta selenium concentrations.** The Bay currently receives its largest selenium load from the Delta, which reflects the mixing of the Sacramento and San Joaquin Rivers, the export of a significant fraction of selenium through the aqueducts, and the transformation and uptake of selenium in the Delta. However, the behavior of selenium in the Delta has been inadequately monitored, and the process-level understanding is limited. A regular monitoring program that includes selenium speciation through a network of stations in the Delta is important to implement.

- ***Corbula amurensis* selenium concentrations and abundance.** The elevated risk of selenium to benthic feeding organisms is strongly tied to efficient uptake by the invasive clam, *Corbula amurensis*. Concentrations in this clam provide a useful indicator of selenium in bay particulates, and it is important that this monitoring be continued in the foreseeable future. At present, these data are not routinely released to the public, and the 1995-2010 were only recently released. Easier access to these data, perhaps on an annual basis would make these more useful to the Bay Delta scientific community and allow interpretation of the influences of selenium loads and hydrology on possible uptake.

  There is also little publicly reported information on its abundance of *C. amurensis* over time. A monitoring program that reports on the abundance of these organisms in units of biomass per unit area, would provide valuable information on the potential contribution to the diet of benthic feeding species.

- **Ocean boundary conditions.** Besides the Delta, another important source of relevance to particulate selenium in the Bay is concentrations in the Pacific Ocean beyond the Golden Gate Bridge. Measurement of ocean particulate selenium values is part of the 2010-2012 sampling plan of the Selenium Characterization Study, but longer term monitoring of this boundary is also recommended.

- **Higher trophic level organism data.** One of the key indicators of impairment due to selenium in the Bay-Delta is the concentration of selenium in the muscle tissue and/or liver of the white sturgeon. However, there is insufficient data to evaluate either the existence of impairment or the evaluation of trends. Moreover, with the apparent enhanced selenium bioaccumulation ability of the clam *Corbula amurensis* it is necessary to quantify the importance of this species to the mixed diet of the white sturgeon.

- **Ongoing selenium modeling support.** Over time, selenium transport cycling in the bay is expected to change, driven by hydrologic variability, Delta modifications, land use changes in the watershed, changing algal species and abundance, and possible changes in the distribution of organisms in the bay. Sustained support of a modeling framework that ties together these elements and can be tested against the data should be an important component of the overall monitoring strategy for the Bay.

Supporting Information in Response to Water Quality Challenges in the San Francisco Bay/Sacramento-San Joaquin Delta Estuary, Unabridged Advanced Notice of Proposed Rulemaking

This document provides responses corresponding to questions identified in the Advanced Notice of Proposed Rulemaking (ANPR) related to selenium on page 29 (referring to the February 2011 unabridged version of the ANPR). The three questions that are supported with new information include the following:

1. What, if any, additional information is available to better characterize selenium sources, loadings and impacts within the watershed of the Bay Delta Estuary?

2. What data, studies, and analytical techniques (for example, models) could be used to improve our understanding of the physical processes, including surface-groundwater interactions, controlling selenium mobilization and transport to and within the Bay Delta Estuary?

3. What data are needed to track selenium impacts in the Bay Delta ecosystem as currently configured, and to evaluate potential impacts of selenium under changed flow and transport conditions into and within the Delta?

In the text below an overview is provided of key data that is relevant, including a review of previously published information related to water quality, biota concentrations, and toxicity, as well as key results of a numerical process model and an updated conceptual model of selenium uptake processes in the Bay Delta Estuary. Through this information an explanation is provided for the patterns of clam concentrations in the Bay that are referred to in the ANPR, but without an explanation of the underlying processes. A summary is also provided of new selenium data currently being collected in North San Francisco Bay (NSFB), constituting a major revaluation of selenium speciation in bay after a gap of ten years. This additional body of information offers valuable insight into the behavior of selenium in the Bay, particularly the influence of long-term, regional-scale changes, such as relating to hydrologic patterns, changing Delta water exports in aqueducts, as well as modification of flows through the Delta to the Bay.

Responses below are grouped according to the questions in the ANPR. More detailed information is provided in a set of technical reports that were earlier prepared in support of the selenium TMDL in NSFB. Electronic versions of these reports are attached to this submission.

1.0 What, if any, additional information is available to better characterize selenium sources, loadings and impacts within the watershed of the Bay Delta Estuary?

Overview of Data Presented

A summary of an ongoing selenium water quality data collection effort in the Bay and Delta and an analysis of toxicity of selenium relevant to fish species found in San Francisco Bay is presented below. The water quality data in particular represent a major new effort at characterizing selenium distribution and speciation in North San Francisco Bay, as well as major external influences, such as the inflows from Sacramento and San Joaquin Rivers, and the oceanic influence beyond the Golden Gate Bridge.

New Selenium Source Characterization Data

The Regional Water Board's 2010 Amendment of Waste Discharge Requirements for San Francisco Bay Region Refineries, Order R2-2010-0057, was adopted in March 2010. It directed the refineries to implement effluent and receiving water selenium characterization studies as set forth in Table 4 of the Order.

The *North San Francisco Bay Selenium Characterization Study Plan (2010–2012)* prepared by the Western States Petroleum Association (WSPA, 2010) provided a detailed description of the number and location of samples, the laboratory analytical methods, and the reporting requirements associated with the characterization study. The Study Plan describes two wet weather and two dry weather sampling events over the two-year (2010-2012) sampling program. The first dry weather and wet weather sampling events were successfully conducted in September 2010 and March 2011, respectively.

The purpose of this report is to summarize the 2010 dry weather findings and compare them to data generated in the 1999 North San Francisco Bay using the same methods. The wet weather samples are currently being analyzed by Dr. Greg Cutter (Old Dominion University).

Study Plan Description

The Study Plan (WSPA, 2010) describes the three types of samples that are required to be collected and analyzed: (1) Transect samples collected along a salinity gradient in the estuary, including locations in the Sacramento and San Joaquin Rivers, (2) Refinery effluent receiving-water samples collected near the effluent outfall to characterize near-field selenium concentrations and speciation; and, (3) Effluent samples collected at a location equivalent to the existing effluent compliance point.

First Year of Water Quality Sampling

The dry weather field sampling of transect and receiving water stations occurred on September 8–13, 2010. Refinery effluent monitoring has taken place on a monthly basis, beginning in September, 2010. Each of these sampling activities is described below.

Transect – Transect samples were collected from 22 sites between a site near the Golden Gate Bridge and the Sacramento River at Rio Vista, CA and the San Joaquin River at USGS gage 757 along salinity increments of approximately 1.5-2 parts-per-thousand (g/l); providing a range of salinities from marine (33 g/l) to fresh (<1 g/l).

Samples were also collected on the Sacramento River at Freeport and on the San Joaquin River at Vernalis. The objective of these samples was to establish new endpoint locations that will be used to establish the boundary conditions for the modeling and analysis efforts.

Refinery Effluent Receiving Water – The objective of the receiving-water sampling is to characterize the mixing characteristics of the discharge and the speciation of the selenium upon initial dilution in the receiving water. Samples were collected from the outfall of each refinery's diffuser. The diffusers are located approximately perpendicular to the flow direction, which changes over time as currents reverse over tidal cycles. Receiving water samples were collected from the zone of initial dilution (ZID) for each discharge, with one being approximately 10m up current and another being approximately 10m down current of each refinery's discharge for a total of three sample locations per diffuser.

The locations of the dry weather sampling stations are presented in Figure 1.

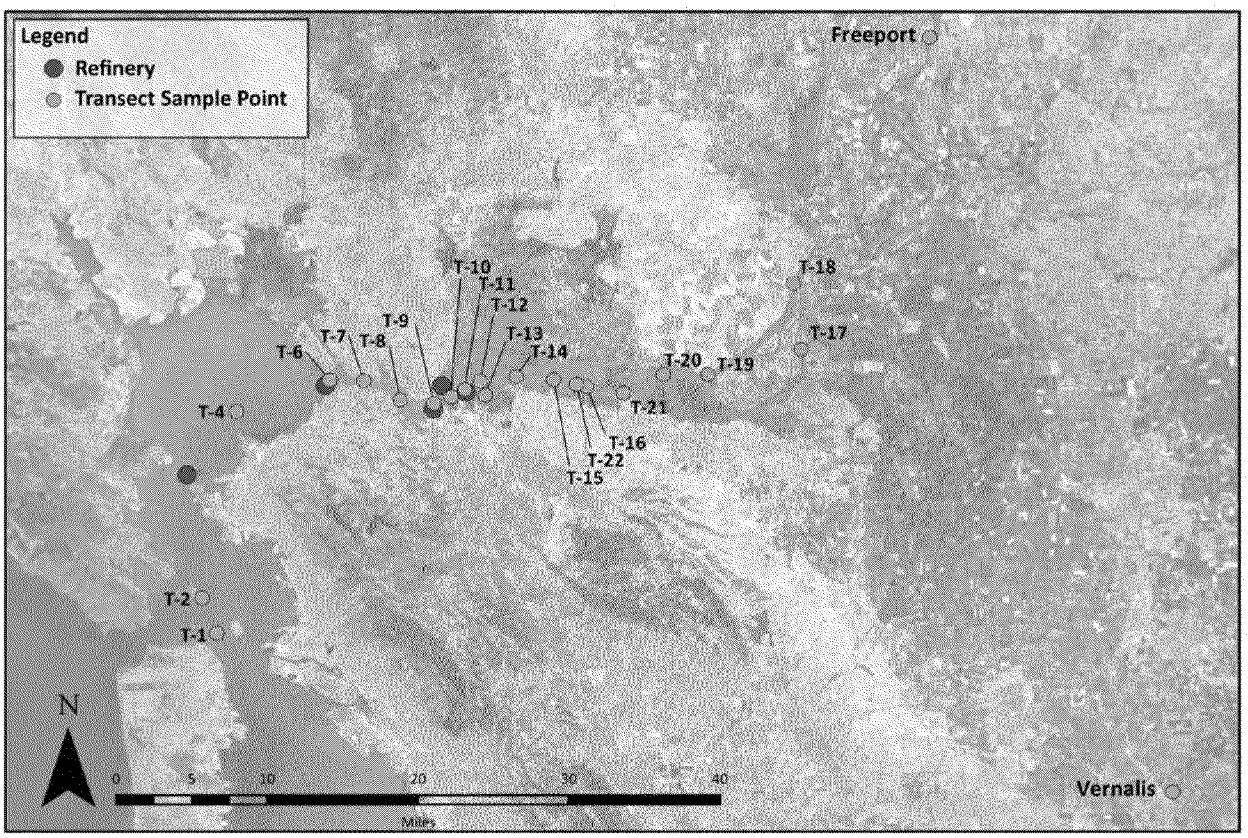

Figure 1 Dry Weather Transect Sample Locations (September 8-9, 2010).

Refinery Effluent – Monthly refinery effluent samples were collected from the fully-treated effluent discharge location. To date, six effluent samples have been collected from the refineries. The objective of these samples is to characterize each refinery's effluent prior to being diluted by receiving water upon discharge.

Water Quality Sampling Results

Concentrations of different selenium species through the estuary transect are presented in Figure 2 through Figure 7, and discussed individually below.

- Selenite data in the dissolved phase are shown along the estuary in Figure 2 (concentrations in the rivers have not been reported). Concentrations exhibit a slight increase from the freshwater end to Central San Francisco Bay (Central Bay). Concentrations exhibit a greater range in 2010 than in 1999, with concentrations in Suisun Bay lower and concentrations in Central Bay higher than the 1999 values.

- Selenate data in the dissolved phase are shown in Figure 3. For this species, there is a clear difference between the 1999 and 2010 sampling, with concentrations nearly half of their 1999 values at several stations throughout the Bay. Overall, selenate concentrations in 2010 are about twice the selenite concentrations.

- Selenide (organic selenium, or Se(-II)) concentrations are shown in Figure 4 and are considerably variable compared to the selenite and selenate values. The 2010 values are higher than the 1999 values, sometimes by a factor of more than two. The 2010 concentrations exhibit a weak spatial pattern, with a similar range of concentrations across the salinity range. In the 2010 sampling, selenide and selenate concentrations are of similar magnitude (about 0.04 μg/l).

Despite the differences in individual species concentrations in 1999 and 2010, total selenium concentrations (Figure 5) for both periods are quite similar, with slightly higher concentrations in the mid-salinity range, and lower and higher concentrations at the freshwater and seawater ends. The riverine boundary concentrations shown in this figure illustrate the difference between the Sacramento and San Joaquin River inflows. Concentrations in Vernalis are about 7 times greater than at Freeport. Figure 5 also shows the concentrations at the three receiving water stations near each refinery outfall.

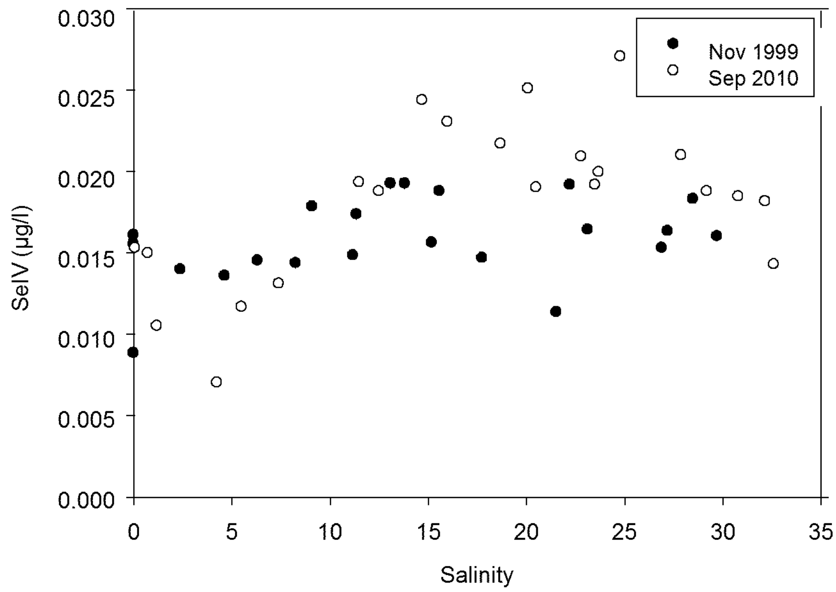

Figure 2 **Selenite (SeIV) concentrations across the estuary with data from November 1999 and September 2010.**

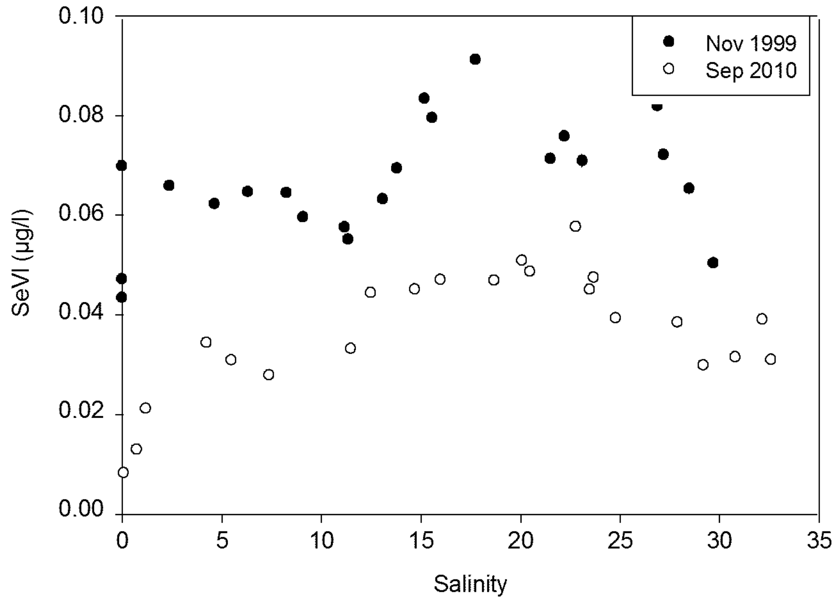

Figure 3 **Selenate (SeVI) concentrations across the estuary with data from November 1999 and September 2010.**

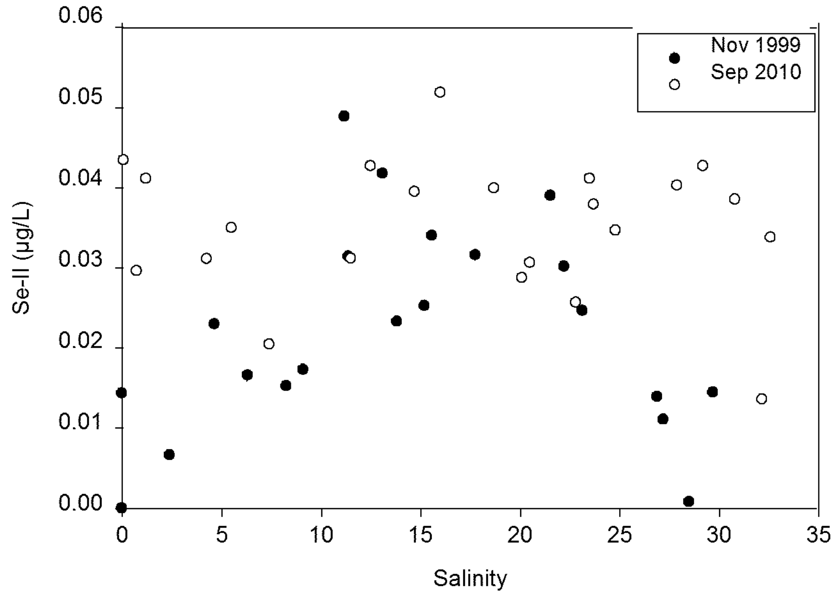

Figure 4 Organic selenium (Se-II) concentrations across the estuary with data from November 1999 and September 2010.

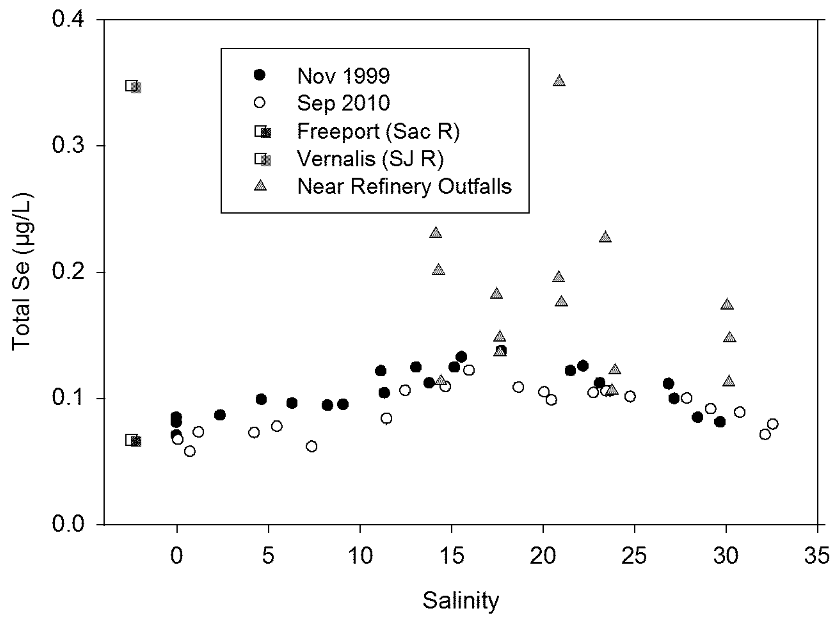

Figure 5 Total dissolved selenium concentrations across the estuary with data from November 1999 and September 2010. Also shown are 2010 data from the riverine sources at Freeport (for Sacramento River upstream of the Delta) and at Vernalis (for San Joaquin River), and stations near the five refinery outfalls

Total particulate selenium concentrations across the estuary (shown as µg/g), including the riverine boundary and refinery outfall sites, are shown in Figure 6. Concentrations in the Bay are lower than observed in the riverine inputs for San Joaquin and Sacramento Rivers. Concentrations in the Sacramento River are approximately half the concentrations in the San Joaquin River. Particulate selenium concentrations in proximity to refinery outfalls are within the range of the estuary concentrations, unlike the case of dissolved selenium concentrations, where they are noticeably higher than the estuary concentrations.

The ratio of the particulate to dissolved selenium concentrations, expressed as a Kd in units of l/g[1], across the estuary, including the riverine boundary and refinery outfall sites, are shown in Figure 7. There is significant decrease in the Kd values between 1999 and 2010, which is expected from the preceding plots because the particulate selenium concentrations are lower, even though dissolved selenium concentrations have not changed much over the period of sampling. Kd values are higher in the Sacramento River than San Joaquin River by a factor of about 3, the values at the low salinity end of the estuary are similar to the Sacramento River values. The refinery values are about the same as or slightly lower than the estuary values at nearby locations.

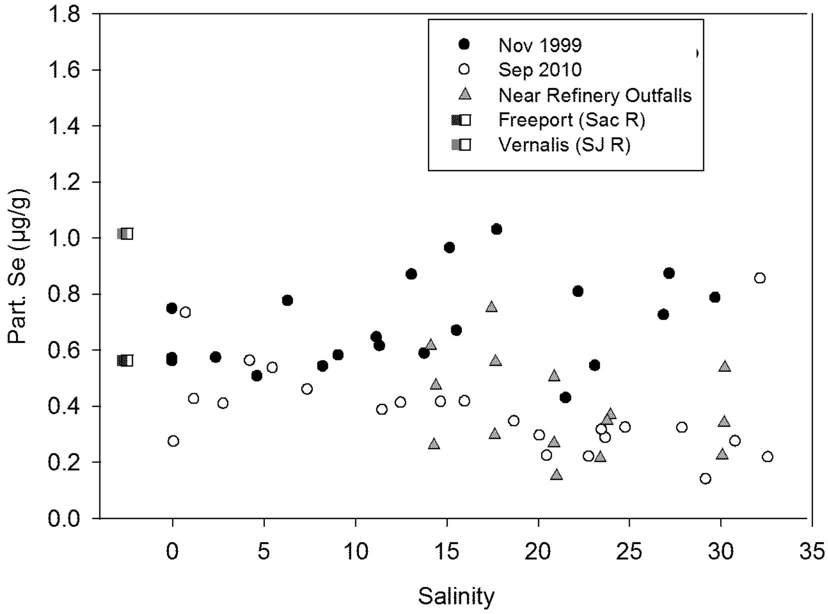

Figure 6 Total particulate selenium concentrations across the estuary with data from November 1999 and September 2010. Also shown are 2010 data from the riverine sources at Freeport (for Sacramento River upstream of the Delta) and at Vernalis (for San Joaquin River), and stations near the five refinery outfalls.

[1] For constituents which can be assumed to be partitioned between the dissolved and particulate phases using an equilibrium-type exchange, Kd is typically termed as the partition coefficient, and is calculated as the ratio of the concentration in the particulate phase to the concentration in the dissolved phase, i.e., (µg/g)/(µg/l). The final units of Kd are thus l/g. It is also reported in units of ml/g, in which case the numerical values of Kd in Figure 4-12 are multiplied by 1,000. Although the interaction of selenium with particulate materials in not truly an equilibrium-type reaction, the Kd value nonetheless provides an instantaneous snapshot of the ratio between dissolved and particulate phases.

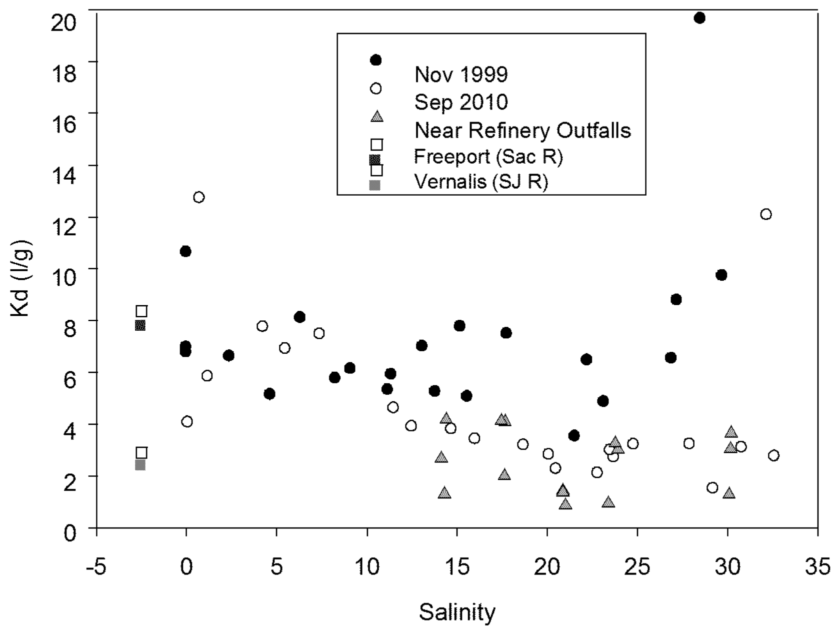

Figure 7 Ratio of particulate to dissolved selenium concentrations (expressed as Kd with units of l/g) across the estuary with data from November 1999 and September 2010. Also shown are 2010 data from the riverine sources at Freeport (for Sacramento River upstream of the Delta) and at Vernalis (for San Joaquin River), and stations near the five refinery outfalls.

Water Quality Preliminary Findings

The discussion presented in this summary report is based on data available to date and is focused on total selenium concentrations in the dissolved and particulate phases, plus speciation in the dissolved phase. Some components of the data that will facilitate interpretation, especially speciation on particulates, are expected to become available soon. However, given the similarity between the last sampling in 1999 and the current sampling, the data obtained in this work can be compared directly with the prior sampling, and allow interpretation of changes over the preceding decade.

The San Joaquin River boundary value of particulate selenium in µg/g is about twice that at Sacramento River at Freeport. The San Joaquin River is widely understood to represent highly contaminated conditions for selenium, and the Sacramento River is thought to represent background conditions. Given this consideration, the range of particulate concentrations is fairly narrow, and because the flow in the Sacramento River is much higher, the role of the Sacramento River needs to be considered in understanding the behavior of selenium in particulates in the system. Compared to the riverine boundary condition (Rio Vista, identified as station T-18 in the 2010 sampling event), particulate concentrations in µg/l at Rio Vista and at Freeport are similar, although concentrations in µg/g are slightly lower at Rio Vista than at Freeport.

Kd values, representing the ratio of particulate to dissolved concentrations, are lower in 2010 than in 1999 by a factor of 2 to 3. This is a significant finding and demonstrates the complexity of selenium uptake by different living and non-living particulate phases. Although a more complete analysis will be performed after the particulate speciation data become available, these calculations show that any given snapshot of selenium distribution in different compartments should be treated with caution, and that the ratio of particulate to dissolved cannot be assumed to remain fixed over changing conditions, which may include, among other things, changing sources, phytoplankton abundance and species, selenium speciation, and also seasonal and long term hydrological changes.

Overall, these samples provide valuable new information on the state of selenium in the estuary and will continue to form the basis of modeling analysis for the selenium TMDL. Additional data in subsequent phases will allow a more complete interpretation of changes in selenium cycling in the Bay. This set of samples contains the first selenium speciation at the riverine boundaries in the Sacramento and San Joaquin Rivers, which are essential for estimating the external loading to the Bay. Subsequent efforts will also include sample collection in the ocean (using an existing cruise from the University of California at Santa Cruz to obtain samples for selenium analysis), and provide information on the ocean boundary, a data gap that has been identified in previous work.

Discussion of Toxicity Data

With the effort that is underway to develop a water quality criterion based on fish tissue concentration, it is important to take a critical look at the key studies that contribute to the selenium toxicity information in general and the information for species considered for evaluation of selenium exposure risk in the Bay Delta. Much of the freshwater fish literature points to a fairly steep zone in the relationship between tissue concentration and effects usually starting somewhere between 10 and 15 ug/g selenium in which fish go from no apparent effects to effects that may be statistically significant compared to controls but may not be biologically significant.

The interpretation of what tissue concentration results in significant effects --and for that matter a No Observable Effect Concentration, NOEC--is very inconsistent among studies. A review of available fish studies (Table 1) suggests that a selenium concentration > 20-30 ug/g in juvenile or larval fish tissue is probably associated with a biologically significant effect such as an EC20 or EC25 in the better, high quality lab or field studies. Specifically, Table 1 presents a summary of some more recent and relevant tissue-based effects levels for selenium taken from the literature. Notably, studies presenting both no effects levels and lowest effects levels on white sturgeon (Linville 2006 and Tashjian et al. 2006) indicate that effects manifest at tissue concentrations between 12 and 22.5 µg/g. In considering effects to Chinook salmon (*Oncorhynchus tshawytscha*) from selenium, it is useful to consider effects reported for other members of this genus. Rainbow trout (*Oncorhynchus mykiss*) was reported to have an EC15 between 8.8 and 10.5 µg/g. Cutthroat trout (*Oncorhynchus clarkii*) were reported to demonstrate no effects to larvae spawned from eggs with selenium concentrations as high has 21.0 µg/g. Although these values are for egg concentrations, they are substantially higher than the value suggested by USFWS.

Table 1
Summary of Relevant Tissue-based Effects Levels for Selenium

Species	Lifestage	Tissue	Highest Se conc with no effect (ug/g)	Lowest Se conc with significant effect (µg/g)	Reported EC20 or EC25	Source
White sturgeon	Larvae		12	20	21.92	Linville (2006)
White sturgeon	Larvae	Whole Body	14.7	22.5	NA	Tashjian et al (2006)
Bluegill	Juvenile		6.7 – 9.4	10.7 – 16.0	Approx. 15	EPA (2008)
Rainbow trout	Embryo		10	15	25.5	Holm et al (2005)
Bluegill	Larvae		19.5	38.4	23.2	Doroshov et al (1992)
Splittail	Juvenile		10.1	15.1	15.1	Teh et al (2004)
Razorback sucker	Larvae		>12.9	>12.9	>12.9	Hamilton et al (2005)
Chinook salmon	Larvae	Whole body	5.3	10.4	NA	Hamilton et al (1990)
Rainbow trout	Larvae	Egg			~EC15 = 8.8 – 10.5	Holm et al (2005)
Brook trout	Larvae	Egg			~EC15 = 8.8 – 10.5	Holm et al (2005)
Cutthroat trout	Larvae	Egg	20.6	46.8	NA	Rudolph et al (2008)
Cutthroat trout	Larvae	Egg	21.0	NA	NA	Kennedy et al (2000)
Northern pike	Larvae	Egg	8.02	NA	NA	Muscatello and Janz (2009)
White sucker	Larvae	Egg	4.89	NA	NA	Muscatello and Janz (2009)

Toxicity information for two species, white sturgeon (*Acipenser transmontanus*) and Chinook salmon (*Oncorhynchus tshawytcha*) is presented below. Additionally, new information is presented on the potential protective effects of selenium against methylmercury toxicity.

White Sturgeon

The Ph.D thesis by Linville (2006) is often cited as a basis for assessing the effects of selenium on the health and the reproduction of white sturgeon in the Bay Delta, and her work points up several of the technical issues involved in developing a selenium fish tissue criterion. For example, Linville used logit analysis to estimate endpoints for selenium tissue concentrations. With only 3 or 4 treatments, such an analysis has fairly high uncertainty and close inspection of most of the figures presented demonstrate an often non-logarithmic relationship and, in most cases, no apparent relationship between tissue concentrations and effects. This was especially true for the edema effect, an occurrence observed in other studies. Linville does not present confidence intervals around the logit equations derived and, based on the data given, these would appear to be very large, especially as one goes below the EC50 (which is where the logit analysis might tend to be most accurate). With the data presented, one could as easily conclude that a selenium tissue concentration in juveniles or larvae of about 20 ug/g is an appropriate concentration to use as an EC20 or even NOEC in some cases. Combining experiments as Linville does in Chapter 3 of her thesis is not warranted for several reasons. Linville used two very different types of Se exposures in experiments: one in which larvae were exposed via maternal transfer from adult fish previously exposed to dietary Se over several months; and other experiments in which larvae were exposed to Se via microinjection of selenium. Linville combined the data from these two types of experiments to calculate different endpoints. Using categorized concentrations of Se observed in larvae at the start of larval development from the different experiments, an average percent mortality was estimated, which was biased because the amount of exposure time elapsed at this point in development differed between the two types of exposures. Also, the categories defined by Linville represented ranges of Se concentrations (e.g., 12 – 16 ug/g), which are not supported by the data, given the different Se analysis techniques used in experiments and the fact that these categories were assigned by the author after the fact. Furthermore, the variability surrounding the mean estimates given in these combined analyses were very high (coefficients of variation were conservatively > 40% in most cases due to very few replicates used in different treatments). Combined data were also used by Linville to calculate EC15, EC25, and EC50 based on structural deformities and edema. Again, the variability surrounding each data point in the figures was not presented but is in fact quite high (CVs > 40% for most data points), yielding highly uncertain relationships with Se concentration. Finally, combining results of fish used in all of these experiments increased statistical power of the analysis for some Se concentration ranges (low Se concentrations especially) more than others, which increases the Type I error rate so that an effect is apparently observed but is likely to be a false positive. Of all the experiments presented, the maternal exposure experiment presented in Chapter 3 is the strongest from an ecological perspective because the method of exposure to eggs and larvae is the most realistic. It should be noted that the endpoints calculated by Linville using logit analysis were substantially higher than those obtained using the microinjection technique. While the latter approach does control for some natural variation in transfer of selenium to eggs, it is very invasive and has dubious relationship to real world exposures. While Linville demonstrates that controls responded acceptably to this treatment, larvae were followed for only a few days (to stage 45). It is unclear whether controls would have in fact matured normally over the next several weeks and months. One other point is that Linville does not characterize water quality anywhere in the thesis, except for temperature and dissolved oxygen. There should be data demonstrating the lack of other potential toxicants that would either further stress the organisms or perhaps heighten the effect of selenium in some way.

In summary, the Linville thesis establishes a link between selenium in parental fish tissue being transferred to eggs and larvae and resulting in substantial deformities at concentrations above about 25 ug/g. The issue is that Linville and some others have attempted to identify either effect levels or NOECs that inherently have high variability and are not defensible based on the data reported.

Chinook Salmon

In a recent report (Beckon and Maurer, 2008), the US Fish and Wildlife Service appears to base their analyses and conclusions on a study of dietary selenium exposure to Chinook salmon by

Hamilton et al (1990). Specifically, USFWS used results presented by Hamilton et al. after 90 days of exposure in freshwater as well as following a 10-day brackish water challenge. There were multiple issues with the Hamilton et al. study that have been discussed in the literature (e.g., DeForest et al. 1999). The two primary issues with this study were: 1) the source of the high-selenium feed in one treatment and 2) high control mortality at the 90-day endpoint.

Exposed fish were fed two different diets which included mosquito fish. One diet consisted of fish caught from a reference area that were spiked with seleniomethionine while the other exposure diet included wild-caught mosquito fish from an agricultural drain that was high in selenium (the San Luis Drain or SLD). The SLD fish generally demonstrated greater sublethal (e.g., growth) effects and this may or may not have been related to unknown contaminants present in this diet. USFWS lumped the results from these two different diets together in their analysis as they felt that the tissue-concentration response was similar between the two. The use of the SLD data is inappropriate for use as it was uncontrolled and almost certainly contained contaminants in addition to selenium.

The experiment presented length, weight, and survival data at 30, 60, and 90 days of exposure. There was substantial mortality of control organisms (33.3% in SLD and 27.5% in seleniomethionine) at 90 days in both studies. Conversely, the results at 60 days were quite good (control mortality of 1% in SLD and 0% in the seleniomethionine). USFWS do not appear to have corrected for this increased control mortality when the 90-day data were used.

For the brackish water experiment, USFWS concludes that a tissue concentration of 7.9 µg/g would result in 15% mortality within 10 days (based on USFWS treatment of the Hamilton et al. 10-day brackish water challenge data). The data derived from the SLD diet demonstrates greater resulting tissue concentrations of selenium in the juvenile salmon (28.8 µg/g vs. 23.2 µg/g) than the seleniomethionine diet. However, the seleniomethionine diet resulted in higher mortality than the SLD diet (76% vs. 43%). The interpretation of the Hamilton data by the USGS has several issues as pointed out above. Further, it is not defensible to base a criterion on a 15% effect because this is statistically and ecologically highly uncertain.

Summary of Toxicity Data

The foregoing discussion of white sturgeon and Chinook salmon selenium toxicity studies underscores many of the technical issues and concerns involved in formulating a scientifically defensible tissue-based selenium water quality criterion. A point estimate endpoint related to clear, unambiguous population-level effects due to selenium toxicity is desirable because it inherently establishes an effect level that will sustain sensitive fish populations while not being over-protective to the point that natural variability in selenium tissue levels or fish responses is considered an impairment. An NOEC approach is not desirable because it does not inherently specify an ecologically relevant effect, but rather a statistically significant effect, which may be more associated with experimental design than biology. Two major concerns with the selenium tissue studies for white sturgeon and Chinook salmon are an insufficient range of treatments and effects with which a defensible point estimate can be established, and the use of biological endpoints such as edema frequency, which has been shown to be highly variable and researcher-dependent. Experiments are needed that target several (at least 5) selenium treatments within the range of 0 – 50 µg/g selenium and the endpoint should be based on mortality or structural deformities that are shown to have high reproducibility. The point estimate level needs to take into account natural as well as experimental variability and therefore should not be based on any effect level less than an EC20. Smaller effect levels are generally not defensible either statistically or ecologically, and an EC20 is typically used when deriving other chronic water quality criteria. In addition, there needs to be consensus on the life stage being targeted for a tissue-based criterion. Different results have been reported in the literature depending on whether tissue concentrations are based on egg, larvae, or juvenile muscle tissue. Much of the recent research has focused on larval selenium concentrations, which appears to be more ecologically relevant than a criterion based on either egg or juvenile selenium measures.

Protective Effects of Selenium

Dietary selenium has been shown to provide protective effects against methylmercury toxicity (Ralston and Raymond, 2010). This research also indicates that selenium is involved in decreasing Hg accumulation in lake fish. There is a high binding affinity between selenium and mercury, and the mercury-selenium complexes formed have low solubility. As a result, the mercury-selenium present in tissues of prey species may not be available for dietary absorption. This relationship between mercury and selenium should be investigated further in the characterization of selenium impacts in the Bay Delta.

Supporting Attachments

Tetra Tech, Inc. 2008. Technical Memorandum #3: North San Francisco Bay Selenium Toxicological Assessment.

Western States Petroleum Association. 2010. North San Francisco Bay Selenium Characterization Study Plan (2010–2012). Submitted to the Regional Water Quality Control Board, San Francisco Bay Region. October 23, 2010.

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2.0 What data, studies, and analytical techniques (for example, models) could be used to improve our understanding of the physical processes, including surface-groundwater interactions, controlling selenium mobilization and transport to and within the Bay Delta Estuary?

A set of analyses in support of the San Francisco Bay Regional Water Quality Control Board's North San Francisco Bay (NSFB) selenium TMDL effort were prepared over 2008–2010. The analyses involved evaluation of the existing scientific literature and existing data in the region, as well as a significant process modeling effort. The analyses are presented in six technical reports. These reports were reviewed by a committee of technical specialists as well as a regional stakeholder group. All reports are in the public domain and available at: http://www.swrcb.ca.gov/rwqcb2//water_issues/programs/TMDLs/seleniumtmdl.shtml

The summary below highlights the main findings of the analyses performed in support of the TMDL.

The published literature on the biogeochemistry of selenium emphasizes the role of speciation in biological uptake. The key forms of selenium in the dissolved phase include selenate (Se+VI), selenite (Se+IV), and organic selenides (Se-II). Particulate phase selenium includes elemental selenium (Se0), as well organic selenides in living and non-living material (Se-II), and sorbed forms of inorganic selenium. The pathway of most concern for biological uptake is the conversion of dissolved selenium to particulate forms, its concentration in the tissues of filter-feeding organisms, and its subsequent availability to higher trophic level organisms.

To develop the TMDL, there needs to be a scientifically reliable approach for relating the loads of selenium to concentrations in water, and then relating the water column concentrations to concentrations in the tissues of key organisms that are a focus of the TMDL. A reliable approach must be able to explain the key features of historical selenium behavior, as well as explain the interactions between different species across seasons and years in a dynamic system such as NSFB, where there are consistent seasonal variations in outflow from the Delta, as well as large year-to-year differences in flow. Although simple representations of selenium behavior are possible, including the use of fixed ratios between two compartments of interest, such as a water column:particulate ratio or water column:clam ratio, such methods are not able to explain *a priori* the range of outcomes that have occurred in the recent past or the range of seasonal differences observed today. Most importantly, this approach is unable to explain the seasonal and the inter-annual behavior of *Corbula amurensis* concentrations in the Bay that have been monitored on a continuous basis since 1994. Referring to this issue, the ANPR states the following on page 32: *"Recently presented data on concentrations of selenium in North Bay clams, which do not show a clear-cut decline in selenium despite reductions in water column concentrations in San Joaquin River water entering the Bay Delta Estuary, suggest that more information is needed to determine the relationship between river inputs and processes in the downstream environment that affect biotic uptake."*

The information provided in this response and supporting documents provides a process-based explanation for the clam concentration data from 1994-2010. The existence of a framework to explain the observed clam concentrations is important from a long term management perspective, where many drivers related to selenium uptake may change, such that ratios between compartments (such as water column:particulate ratio or water column:clam) may not be assumed to remain constant. Large scale changes that could be important include changing algal populations and species composition, changes in the food web, and changes in flows through the Delta with the outflow containing a different percentage of San Joaquin River flows than at present.

Evaluation of Selenium Sources

The quantification of selenium loadings from different point and non-point sources including Sacramento River and San Joaquin River inputs through Delta, local refineries, POTWs, tributaries and sediments, during both dry and wet seasons, was the first component of this analysis (See attached document: *Technical Memorandum 2 North San Francisco Bay Selenium Data Summary and Source Analysis*). Although selenium speciation in the Bay is not monitored in a systematic manner, there are several ongoing programs in the region that monitor some form of selenium (typically total dissolved selenium) at selected locations. These data were the basis of the load estimates developed in the aforementioned document.

The analysis of sources indicated that the annual loadings from the Central Valley through the Delta are the largest source of selenium with high variability depending on total flow through the Delta. Loads in high flow years are estimated to be more than ten times higher than in low flow years. The average Delta load is estimated to be 3,962 kg/yr. Local tributaries draining both urban and non-urban areas, although contributing lower flows than the Sacramento and San Joaquin Rivers, have high selenium concentrations, and are also a large source of selenium during the wet months (estimated average load of 354-834 kg/yr). Refineries are estimated to contribute ~550 kg/yr to NSFB, although these loads were higher prior to the late 1990s when wastewater controls were installed. The point source loads (the refineries and the POTWs) contribute relatively uniform loads over the year, although the non-point source loads (the Delta and the local tributaries) contribute substantially more load in the wet season than in the dry season.

Model Framework

The fate, transport, and biological uptake of selenium in the Bay-Delta system are influenced by intra- and inter-annual flow variability, and selenium transformations among different dissolved and particulate forms. To represent these processes, an estuary model was used to simulate the selenium concentrations in the water column and bioaccumulation of selenium in the NSFB (ECoS3 model, Harris and Gorley, 2003). The model built upon the previous work of Meseck and Cutter (2006) and was applied in one-dimensional form to simulate several constituents including salinity, total suspended material (TSM), phytoplankton, dissolved and particulate selenium, and selenium concentrations in bivalves and higher trophic organisms.

Selenium species simulated by the model include selenite, selenate, and organic selenide. The particulate species simulated by the model include particulate organic selenium, particulate elemental selenium, and particulate adsorbed selenite and selenate. The uptake of dissolved selenium by phytoplankton includes uptake of three species (selenite, organic selenide and selenate). The interactions between these species are represented as first-order reactions, with rate coefficients estimated through calibration in NSFB (Figure 8). Bioaccumulation of particulate selenium to the bivalves was simulated using a dynamic bioaccumulation model (DYMBAM, Presser and Luoma, 2006), applied in a steady state mode. Bioaccumulation into bivalves considers the different efficiencies of absorption for different selenium species (Figure 9). Bioaccumulation to higher trophic levels of fish and diving ducks is simulated using previously derived linear regression equations by Presser and Luoma (2006), and estimates of trophic transfer factors summarized from the literature (Presser and Luoma, 2009).

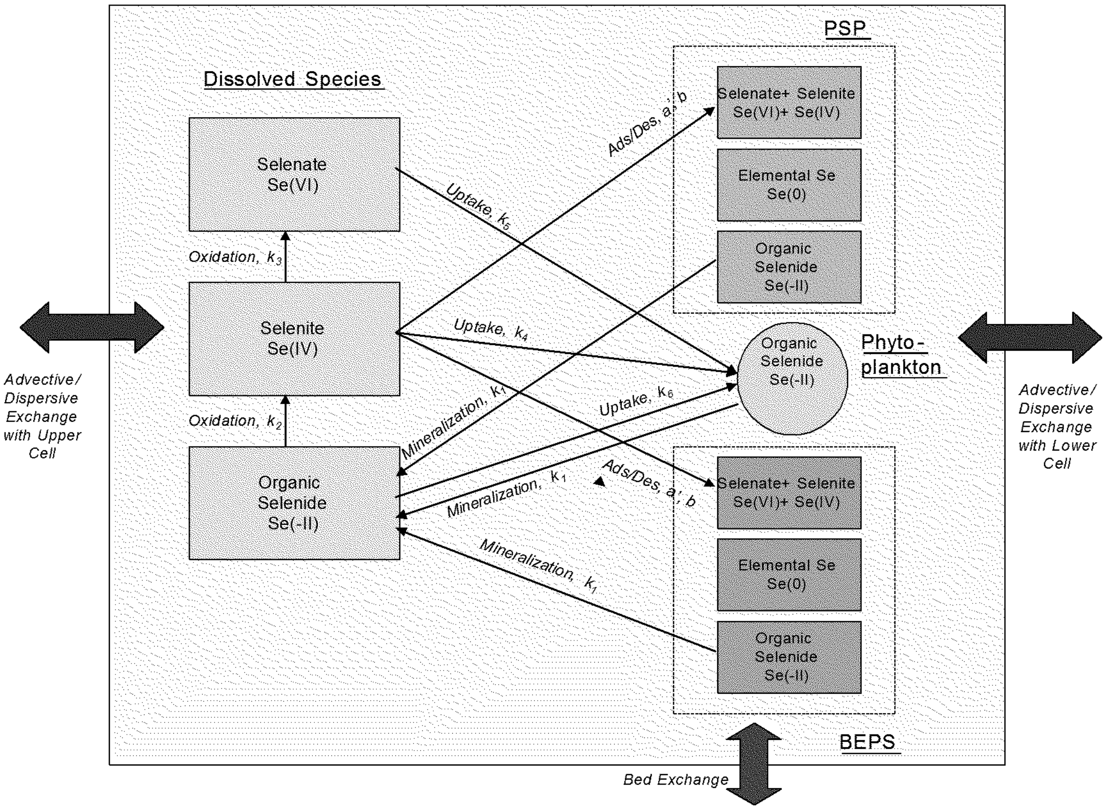

Figure 8 Representation of selenium exchanges between different compartments in each cell of the model. Transformations are shown for each species in the dissolved and particulate phases (PSP, permanently suspended particulates; phytoplankton; and BEPS, bed exchangeable particles). Bivalves consume particulate selenium that is a mix of PSP, BEPS, and phytoplankton.

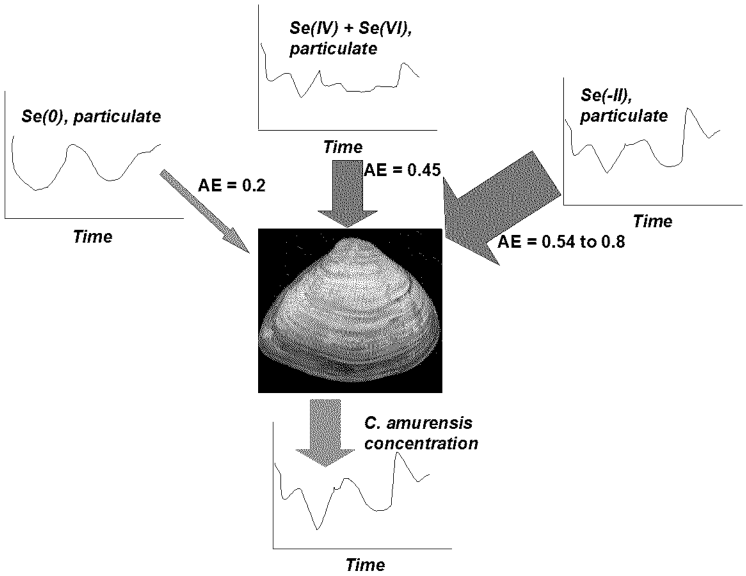

Figure 9 Representation of uptake by clams. The assimilative efficiency (or AE) is a function of the form of the particulate selenium. The highest AE is for organic selenium (Se-II), as would be associated with living and non-living material, and the lowest if for elemental selenium (Se (0)). See Tetra Tech (2010) for detailed literature references for these AE values.

Detailed information on model development, calibration, evaluation, sensitivity evaluation and application to future scenarios is presented in attached document titled *TM-6: Application of ECOS3 for Simulation of Selenium Fate and Transport in North San Francisco Bay.* The model encapsulates a great deal of information about the behavior of NSFB, relating to constituents that influence selenium, such as flows and salinity, suspended particulates, and phytoplankton abundance. These ancillary constituents, unlike selenium speciation, are monitored consistently throughout the Bay by the US Geological Survey (USGS). Important model inputs for which data were available over a simulation period of 1999-2006, include flows in the rivers and local tributaries, chlorophyll a concentrations, suspended solids concentrations, salinity, and total selenium in the rivers and point sources. Data on selenium speciation (in the dissolved phase and in the particulate phase) on selected loads (refineries and riverine sources) were available primarily for 1999 at time of model development. It is important that the model be updated with the new data being collected over 2010-2012, and described in response to Question 1 of the ANPR, and presented in Figures 2 through 7.

Key Features of Bay Conditions

The distribution of selenium across the Bay is discussed in the context of the model calculations. Loads in NSFB are described for 1999, a year for which there are data from a variety of sources, and which is representative of current levels of point source loading. Estimated loads are shown for total selenium as well as for particulate selenium for 1999 in Figure 10. As noted above, non-point sources constitute a large fraction of the external total selenium loads, and are the primary external source of particulate selenium loads. These loads vary by season and by year driven largely by variations in flow in the principal rivers (Sacramento and San Joaquin) and local Bay tributaries.

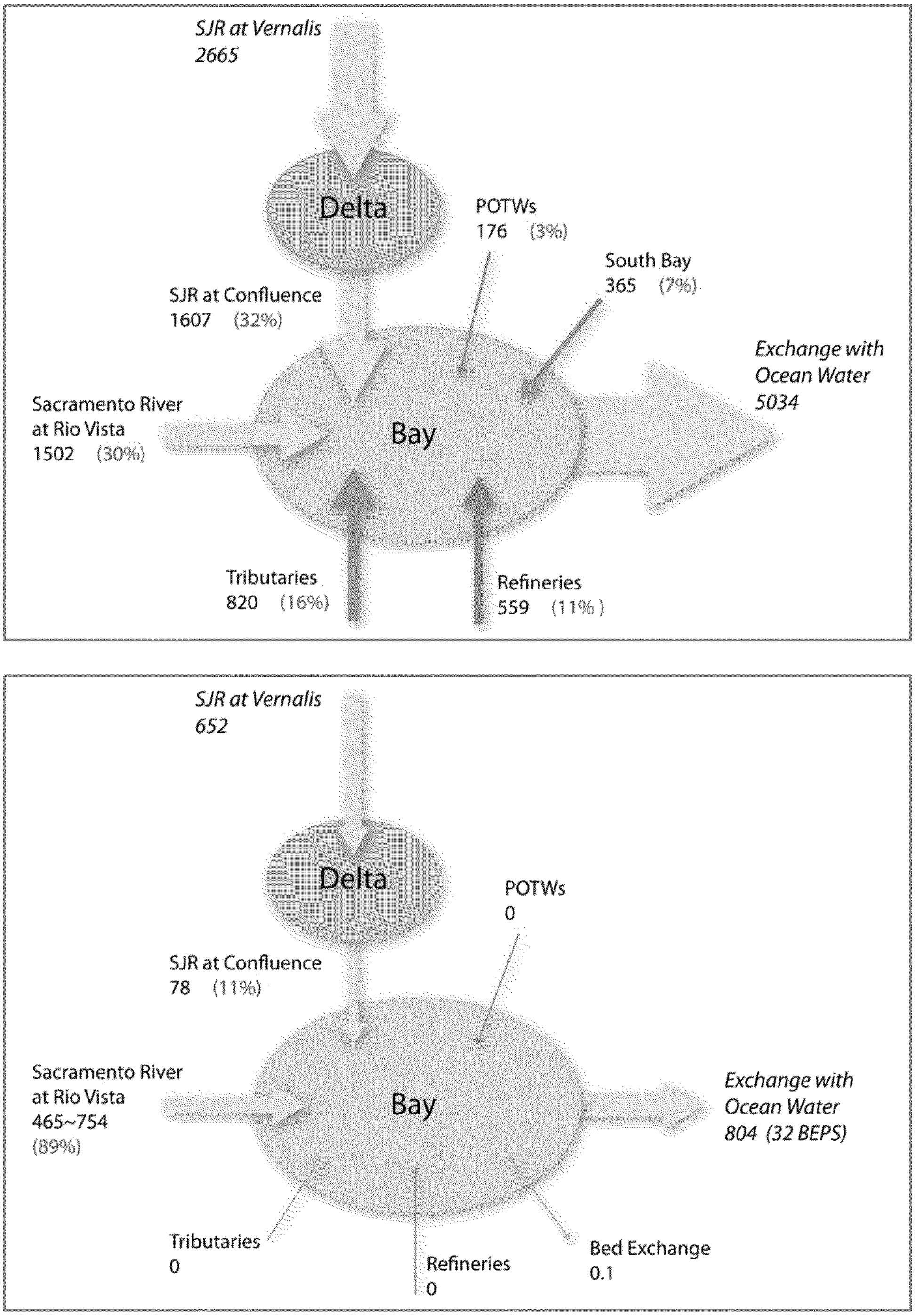

Figure 10 Loads of selenium in San Francisco Bay in kg for 1999: total selenium (upper panel) and particulate selenium (lower panel).

Also important to consider is the variation in total suspended material (TSM) in the Bay water column between the wet and dry seasons. TSM includes mineral rich particles as well as particles of biological origin, such as living and non-living phytoplankton. Values of TSM are shown in Figure 11 for a wet weather day and for a dry weather day in 1999. On the dry weather day, the concentration of TSM from the Delta is relatively high (40 mg/l), but decreases rapidly through Suisun Bay and Carquinez Strait to 10 mg/l. In contrast, on a wet weather day in the same year, the outflow concentration from the Delta is similar (45 mg/l), but the concentrations in Carquinez Strait are much higher (62 mg/l). The difference is caused by the higher outflow volumes from the Delta on the wet weather day, with high sediment concentrations. Using data such as these, the behavior of suspended material in the Bay can be conceptualized as shown in Figure 12 . The suspended material originating in the riverine sources, which is higher in mineral content, tends to settle as the flows enter the Bay. The contribution of the in situ generated particles, primarily phytoplankton, increases as a share of the total particulate load as one travels from the riverine to the ocean end.

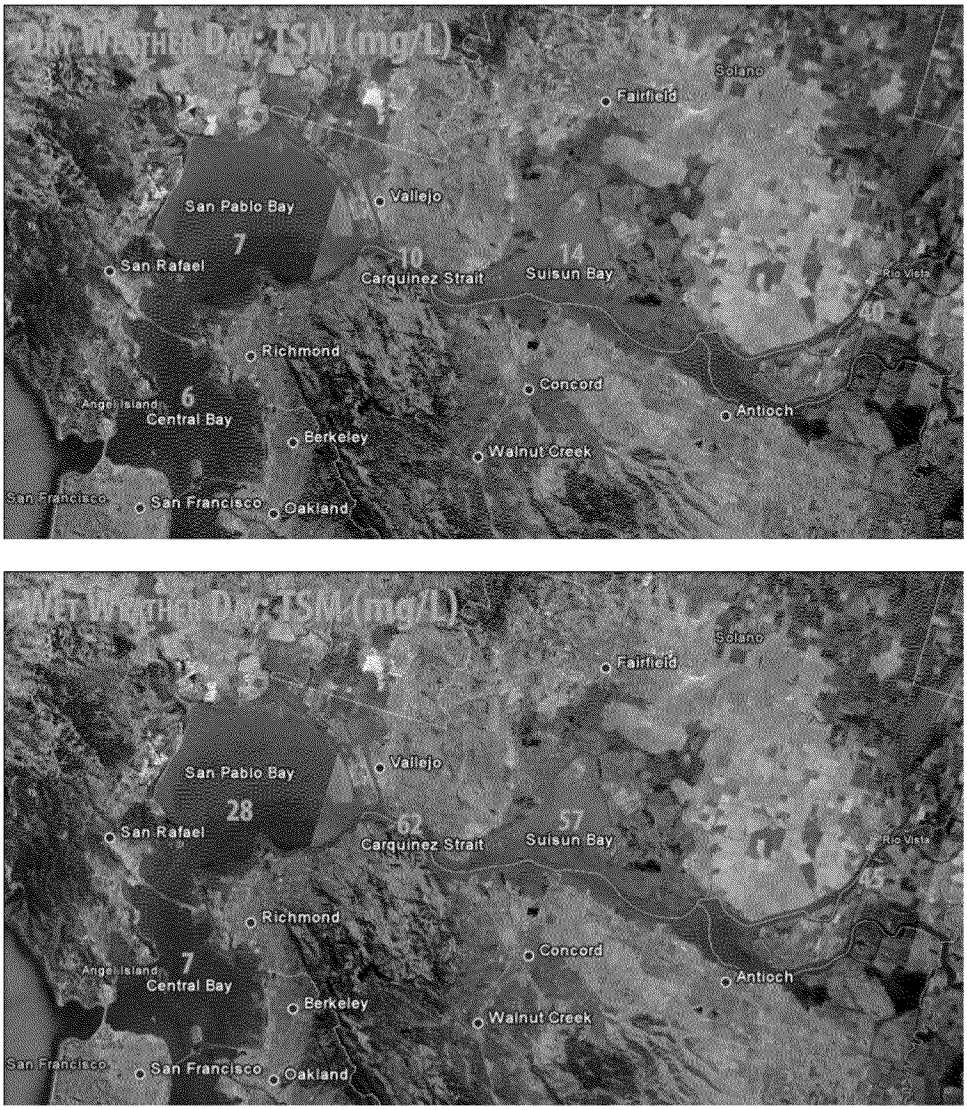

Figure 11 Modeled total suspended material (TSM) from Rio Vista to Golden Gate for a dry weather day and a wet weather day for an average flow year (1999).

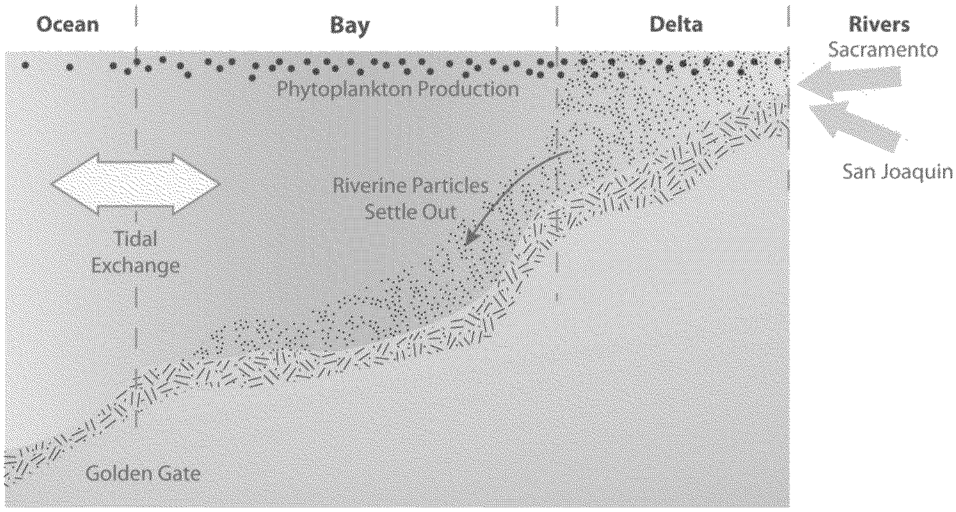

Figure 12 Behavior of suspended particulates in the Delta and Bay.

The overall behavior of particulates also influences the distribution of particulate selenium in the Bay as shown in Figure 13. In this figure, the mix of particulate selenium forms (organic, inorganic, and elemental) is shown across the estuary for the same dry and wet weather days that were used in Figure 11. In both cases, the fraction of organic selenium increases from the riverine to the oceanic boundary, driven by the settling of mineral particles and the increasing relative share of organic particles. In the dry season, especially in Suisun Bay, Carquinez Strait, and San Pablo Bay, the fraction of organic selenium is higher. As shown in Figure 9, the higher organic fraction is indicative of greater assimilative efficiency by clams.

Finally, the ratio of dissolved and particulate selenium can also be examined over time and across the estuary. The changing mix of suspended particles, i.e., mineral versus organic particles, also affects the concentration of selenium expressed as µg/g because the organic fractions, especially algal cells can be richer in selenium. Thus, the ratio of particulate to dissolved concentrations (termed Kd, as discussed in the response to Question 1) increases as the organic fraction of the suspended particles increases. This is shown in Figure 14 where the Kd values are shown for a dry weather and a wet weather day in 1999. The Kd values increase from the riverine to the oceanic end, and are higher in the dry season when the mineral component of the particulates are lower.

Even as the significant changes in the particulate selenium speciation and Kd occur in space and across seasons, the dissolved concentrations vary over a narrow range in both the dry and wet weather days: 0.07 to 0.088 µg/l and 0.077 to 0.103 µg/l respectively (values shown in Figure 14). The role of the distribution of particulates is shown in conceptual form in Figure 15. In the dry season, the contribution of riverine particulate selenium is small relative to the in situ generation of phytoplankton. These conditions also result in higher particulate selenium concentrations (in µg/g). In the wet season, the contribution of riverine particulates is larger relative to in situ generation, and the overall particulate composition is more mineral and lower in selenium concentration. Of course, the riverine contributions of particulate selenium change from year to year, with resulting consequences on concentrations in the Bay.

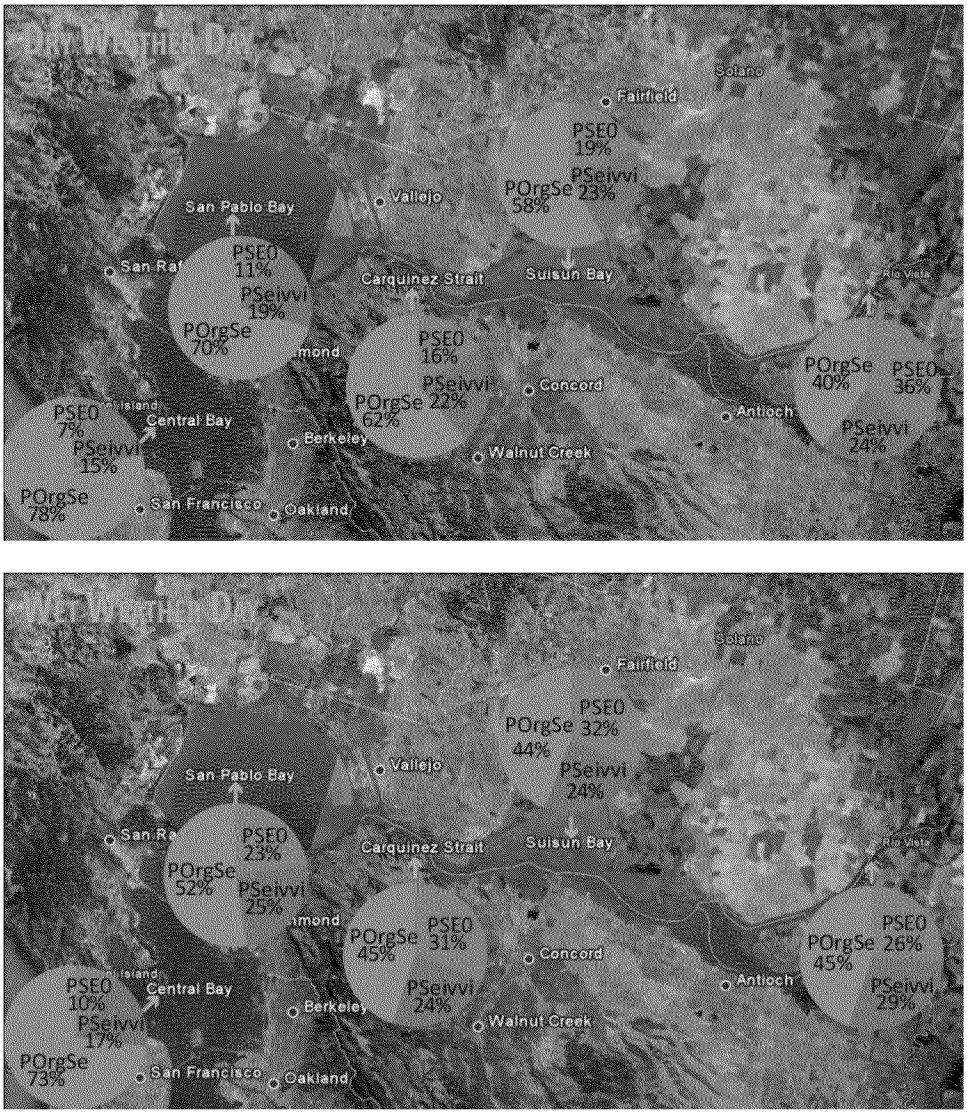

Figure 13 Modeled particulate selenium (PSEO = elemental selenium; PSeivvi = inorganic selenium; POrgSe = organic selenium) from Rio Vista to Golden Gate for a dry weather day and a wet weather day for an average flow year (1999).

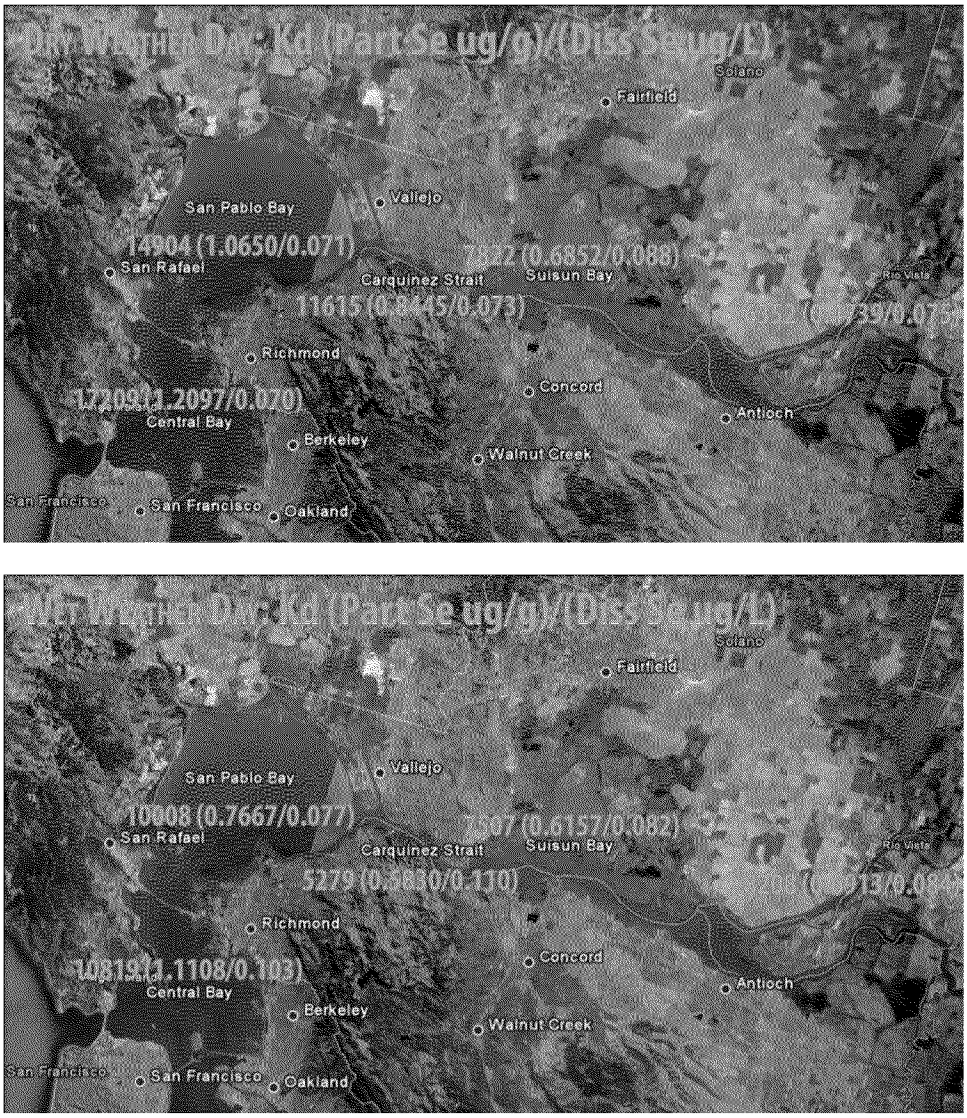

Figure 14 Modeled Kd and particulate and dissolved selenium from Rio Vista to Golden Gate for a dry weather day and a wet weather day for an average flow year (1999).

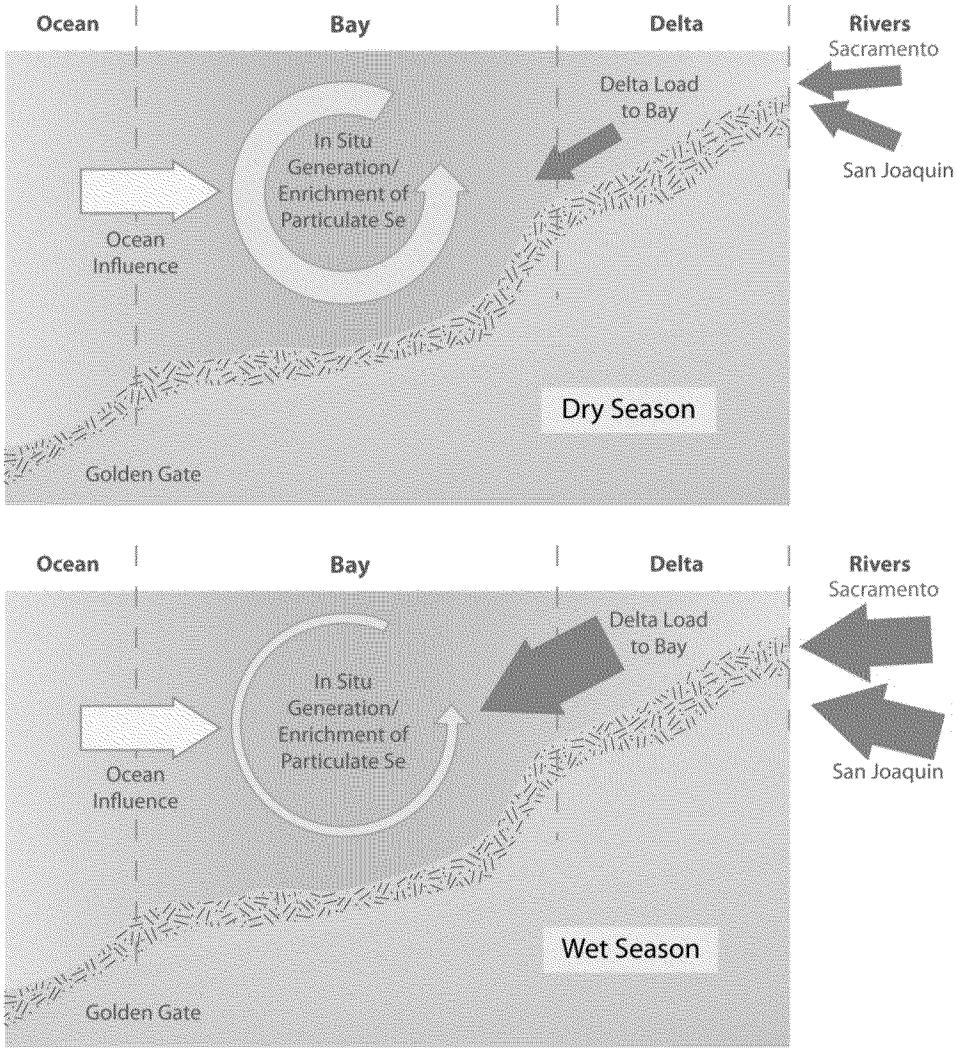

Figure 15 Cycling of particulate selenium in the dry season (upper panel) and the wet season (lower panel).

Ability to Explain Selenium Behavior in the Estuary

The above summary of selenium cycling, embodied in the NSFB selenium model is best illustrated by the use of the model for explaining the 15-year clam data set in the Bay (Kleckner et al., 2010), representing a period with changing hydrology and loads, particularly decreases in refinery wastewater loading beginning in 1998, and a general reduction in San Joaquin River loads through selenium source control actions in the San Joaquin River watershed. Over this period of record, two features stand out in the clam data: there has not been a large reduction in clam concentrations despite the load changes, and there is a significant amount of inter-seasonal variability, with the lowest concentrations in each year occurring during the high flow months, and the highest concentrations occurring in the low flow months. Seasonal high concentrations are almost a factor of two as high as the low concentrations. The seasonal pattern in clams is a feature of the data that cannot be explained by the dissolved selenium concentration data alone, as the dissolved data do not show a similar seasonal pattern.

The NSFB selenium model was applied using measured riverine inflows, as well as using the calibrated parameters for selenium transformation based on the 1999 speciation data, and uptake rates and assimilation efficiencies for different selenium species. A reduction in point source loads, through improved refinery wastewater treatment, is also included in the model inputs. The resulting calculation is shown in Figure 16 and compared against the observed data. The model is able to capture key features of the data very well, including seasonal and inter-annual variations. Changes in clam selenium concentrations from one year to the next are influenced significantly by hydrology, with wet years (such as 2005 and 2006) resulting in lower clam concentrations. The ability to explain this temporal clam behavior is important in itself and also provides insight into future changes in the Bay, where flow modifications in the San Joaquin River or the Delta may result in riverine inputs that differ from historical, both in volume and in the amount of particulate selenium represented by the relative proportion of Sacramento and San Joaquin River flows.

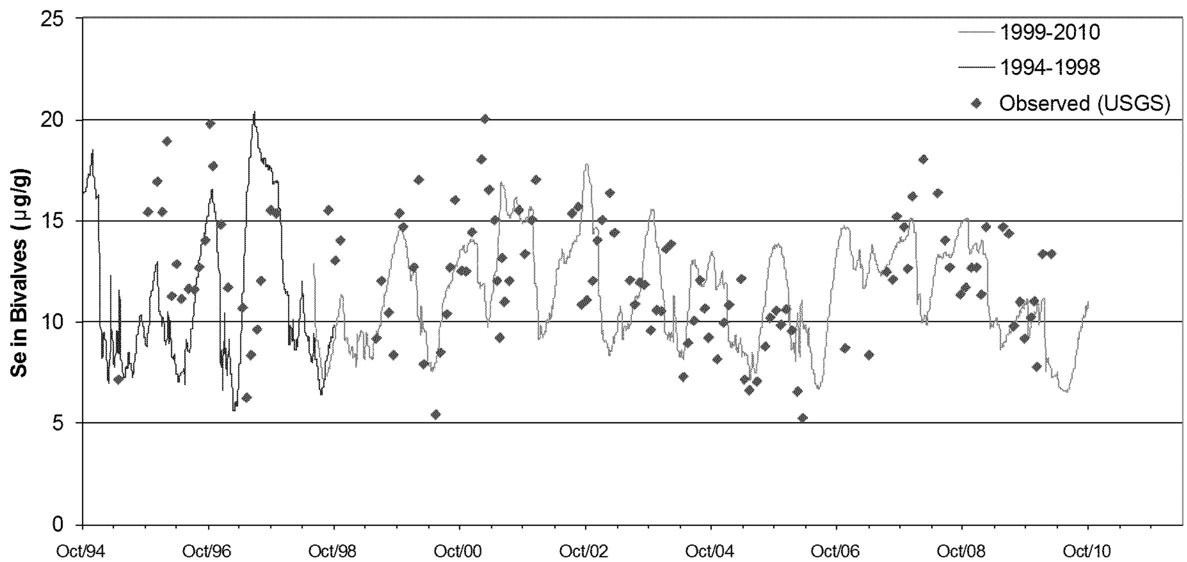

Figure 16 Simulated selenium concentrations in bivalve *Corbula amurensis* compared to long-term data from USGS at the Carquinez Strait for the period of 1994-2010 (Kleckner et al. 2010). Flow data used: DAYFLOW records; Refinery data used: daily data for 1999-2007, constant loads after 2007; San Joaquin River Selenium: observed data at Vernalis, multiplied by Delta removal constants with fixed speciation: SeIV: 0.028; Se VI: 0.658; OrgSe: 0.314.

Why a Complex Model is Needed

The model computations of dissolved and particulate selenium could be compared with a somewhat simpler published approach based on linear partitioning between dissolved and particulate phases (Presser and Luoma, 2006, 2010). The Presser and Luoma approach is easy to explain to stakeholders and is relatively transparent, which are clearly valuable assets in a TMDL-setting process. However, the model does not fully capture the processes associated with particulate selenium uptake and transport, which influence the results obtained for load changes from the current situation. In the linear partitioning approach a reduction in dissolved concentrations results in a proportional reduction in particulate concentrations, a result that is different from the ECoS dynamic uptake/mineralization approach and consideration of external particulate sources. In particular the more complex approach illustrates that there is a floor in particulate concentrations set by the Sacramento River outflows, and that changes to dissolved concentrations alone, such as through the controllable sources in the Bay and San Joaquin River watershed will not achieve a bay-wide reduction in particulate selenium below the floor set by the Sacramento River.

The ability to explain the clam data presented above is a key advantage of the use of a more process oriented model that can be applied in settings where there are many changing factors, and where the assumption of a constant Kd ratio is not valid. In this specific case, for example, there is a systematic two-fold increase in clam selenium concentrations from the wet to the dry seasons each year, that is not related to the dissolved phase concentrations which are relatively uniform. A process-based explanation using the contribution of riverine particulates to the Bay provides a reasonable explanation, and can capture the essence of the changes over time.

Selenium issues in the Bay have been studied for nearly three decades, and management of selenium will be a long term effort, during which many changes in the Bay-Delta system can be expected. To best address these future conditions, it is important to develop tools, such as the one presented here, to capture the greatest amount of process detail that is possible. The application of a process-based model does not completely reduce the uncertainty associated with future projections, but it does provide a robust scientific basis upon which projections can be made.

Supporting Attachments

Tetra Tech, Inc. 2008. Technical Memorandum #2: North San Francisco Bay Selenium Data Summary and Source Analysis.

Tetra Tech. 2010. Technical Memorandum 6: Application of ECoS3 for the Simulation of Selenium Fate and Transport in North San Francisco Bay.

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3.0 What data are needed to track selenium impacts in the Bay Delta ecosystem as currently configured, and to evaluate potential impacts of selenium under changed flow and transport conditions into and within the Delta?

In the ANPR discussion of water quality standards in the Bay Delta Estuary related to selenium, it is noted that the efforts underway will use data on affected species. The Presser-Luoma ecosystem-based model that accounts for food web processes and site-specific conditions is also identified as a tool that will be used in this effort. Although a variety of data from field sampling exists that have been used to either evaluate the existence of environmental impairment or that have already served as a basis of parameterizing the Presser-Luoma model, there is a need to develop a focused monitoring approach to develop information that can be used to establish existing conditions in the Bay Delta with respect to the effects of selenium. This information will also serve as a basis for measuring change to the system and to gauge the effects of ecological forcing factors such as changes in food-web structure, flow conditions, and differences sources and forms of selenium to the system. While there have been several efforts to develop conceptual models of selenium behavior in the Bay Delta Estuary (ref), numerous gaps exist in either the knowledge of the relative importance of identified factors or in the completeness of the data that can be used to model the ecosystem. The risks of having insufficient data to conduct the planned modeling and analyses include the selection of values from sparse or incomplete data sets that support the existing concepts regarding both the relative importance of factors that affect the system and the existence of impairment.

The data needs are best classified into the following sections, each of which is described below: Delta selenium concentrations, *Corbula amurensis* selenium concentrations and abundance, ocean boundary conditions, higher trophic level organism data, and a sustained selenium modeling effort.

Delta selenium concentrations. The Bay currently receives its largest selenium load from the Delta, which reflects the mixing of the Sacramento and San Joaquin Rivers, the export of a significant fraction of selenium through the aqueducts, and the transformation and uptake of selenium in the Delta. However, the behavior of selenium in the Delta has been inadequately monitored, and the process-level understanding is limited. To be specific, there are very few measurements of selenium within the Delta, and aqueduct exports are poorly characterized because the detection limits are too high. None of the routine monitoring, including at the major riverine inflows at Freeport (on Sacramento River) and Vernalis (on San Joaquin River) consists of any speciation of selenium, including a basic separation into dissolved and particulate selenium. An understanding of selenium through this region is all the more important because there is a possibility that the Delta may be reconfigured to deliver more Sacramento River water to the aqueducts, in effect increasing the supply of San Joaquin River to the Bay. San Joaquin River selenium concentrations are roughly 10 times higher than the Sacramento River, and the modeling presented in Tetra Tech (2010) indicates substantially increased concentrations in the Bay if a greater fraction of Delta outflow were to be comprised of San Joaquin outflow. For this reason, a regular monitoring program that includes selenium speciation through a network of stations in the Delta is important to implement.

Corbula amurensis selenium concetrations. The elevated risk of selenium to benthic feeding organisms is strongly tied to efficient uptake by the invasive clam, *Corbula amurensis*. Concentrations in this clam provide a useful indicator of selenium in Bay particulates, and it is important that this monitoring be continued in the foreseeable future. At present, these data are not routinely released to the public, and the 1995-2010 were only recently released (Kleckner et al., 2010). Easier access to these data, perhaps on an annual basis would make these more useful to the Bay scientific community and allow interpretation of the influences of selenium loads and hydrology on possible uptake.

Corbula amurensis abundance. The clam *Corbula amurensis* is thought to be an important part of the diet of benthic-feeding organisms. However, there is little publicly reported information on its abundance over time. A program, perhaps tied to the existing clam selenium monitoring program, that also reports the abundance of these organisms in units of biomass per unit area, would provide valuable information on the potential contribution to the diet.

Ocean boundary conditions. Besides the Delta, another important source of relevance to particulate selenium in the Bay is concentrations in the Pacific Ocean beyond the Golden Gate Bridge. Although the suspended material concentrations in the ocean are lower than in the estuary, particulate selenium concentrations (measured as μg/g) may not follow the same pattern. Measurement of ocean particulate selenium values is part of the 2010-2012 sampling plan, but longer term monitoring of this boundary is also recommended.

Higher tropic level organism monitoring data. There are existing monitoring efforts to determine fish and bird egg concentrations of selenium, conducted by different agencies around NSFB, although it is not clear if these are part of a formal monitoring program. The data are also not readily available. There needs to be an effort to coordinate the existing programs and perhaps make the information available in a central repository, along with information relating to clams and water quality.

One of the key indicators of impairment due to selenium in the Bay-Delta is the concentration of selenium in the muscle tissue and/or liver of the white sturgeon (Linville, 2006). While, as noted in the response to Question 1, there is uncertainty regarding the toxicity endpoint, the information on the concentrations of selenium in white sturgeon is incomplete. Based on the review of existing information, over a period of 13 years (1997 – 2009) 122 measurements of selenium in the muscle tissue of white sturgeon have been made (Table 2). The average concentration of selenium in the fish-tissue samples exhibit a relatively small range (4.3 to 10.4 mg/g-dw) over the Bay Delta, and the coefficient of variation (a gauge of sample-value variability, standard deviation/mean) is relatively small for environmental sample. However, given the differences in the size of the fish included in the different samples and the small sample size there is insufficient data to evaluate either the existence of impairment or the evaluation of trends.

With the planned use of the Presser-Luoma ecosystem model for deriving a water quality criterion for selenium in the Bay Delta, data on the diets of the fish such as the white sturgeon will be important in developing field-derived trophic transfer factors. For example, with the apparent enhanced selenium bioaccumulation ability of the clam *Corbula amurensis* it is necessary to quantify the importance of this species to the mixed diet of the white sturgeon. The existing information on the relative importance of all molluscs in the diet of white sturgeon was summarized by Beckon and Maurer (2008) and is summarized in Table 3. These data indicate that molluscs can be a significant but highly variable contribution (generally below 50%) to the mixed proportion of the prey of white sturgeon. However, with the increase in the population of *C. amurensis* in the Bay Delta there is a concern that a dietary shift and an increase in the importance of this prey item of white sturgeon will lead to an increase in the bioaccumulation of selenium in the white sturgeon. For example, citing Feyrer et al (2003), Stewart et al (2004) note that since the introduction in 1986, *C. amurensis* has been a dominant food item in the digestive tracts of benthivorous sturgeon. However, while Feyrer et al (2003) reported on changes in the diets of 12 species of fish in Suisun Marsh, they did not present any data for the dietary preferences of the white sturgeon. New data on the importance of *C. amurensis* in the diet of white sturgeon as well as the abundance of the clam population is needed in the assessment of selenium impacts in the Bay Delta ecosystem.

Ongoing selenium modeling support. Over time, selenium transport cycling in the Bay is expected to change, driven by hydrologic variability, Delta modifications, land use changes in the watershed, changing algal species and abundance, and possible changes in the distribution of organisms in the Bay. Sustained support of a modeling framework that ties together these elements and can be tested against the data should be an important component of the overall monitoring strategy for the Bay.

Table 2
Summary of available measurements of Se in the muscle tissue of white sturgeon.

Location	Year	Sample Size	Avg. Fish Muscle Tissue Concentration µg/g-dw	C.V. (%)	Fish Length (cm.)	
					Min.	Max.
San Pablo Bay	1997	7	6.3	74	117	145
	2000	6	8.3	41	115	149
	2002	3	8.9	37	91	126
	2003	2	4.3	20	122	137
	2004	14	8.0	36	128	171
	2006	6	5.8	50	-	-
	2009	6	8.7	57	-	-
North Bay	2003	20	4.9	30	61	110
	2004	2	10.4	16	126	150
South Bay	1997	6	4.6	46	117	149
	2000	4	6.7	22	121	182
	2003	5	8.0	59	117	163
	2009	7	4.6	33	-	-
Baywide	2000	15	9.2	76	123	171
	2001	17	10.1	48	127	158

Table 3
Percent frequency of occurrence of molluscs in esophageal and stomachs of white sturgeon (sample size). Data from Tables 8 -10 Beckon and Maurer (2008)

	Fall	Winter	Spring	Summer
Suisun Bay and Carquinez Strait, 1965 - 1967	77 (41)	44.9 (15)	21.1 (59)	40.7 (27)
San Pablo Bay, 1965 - 1967	33.0 (39)	14.9 (49)	14.7 (99)	42.2 (35)
Sacramento-San Joaquin Delta, 1963 1964	0.1 (42)	< 0.1 (13)	< 0.1 (27)	< 0.1 (23)

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